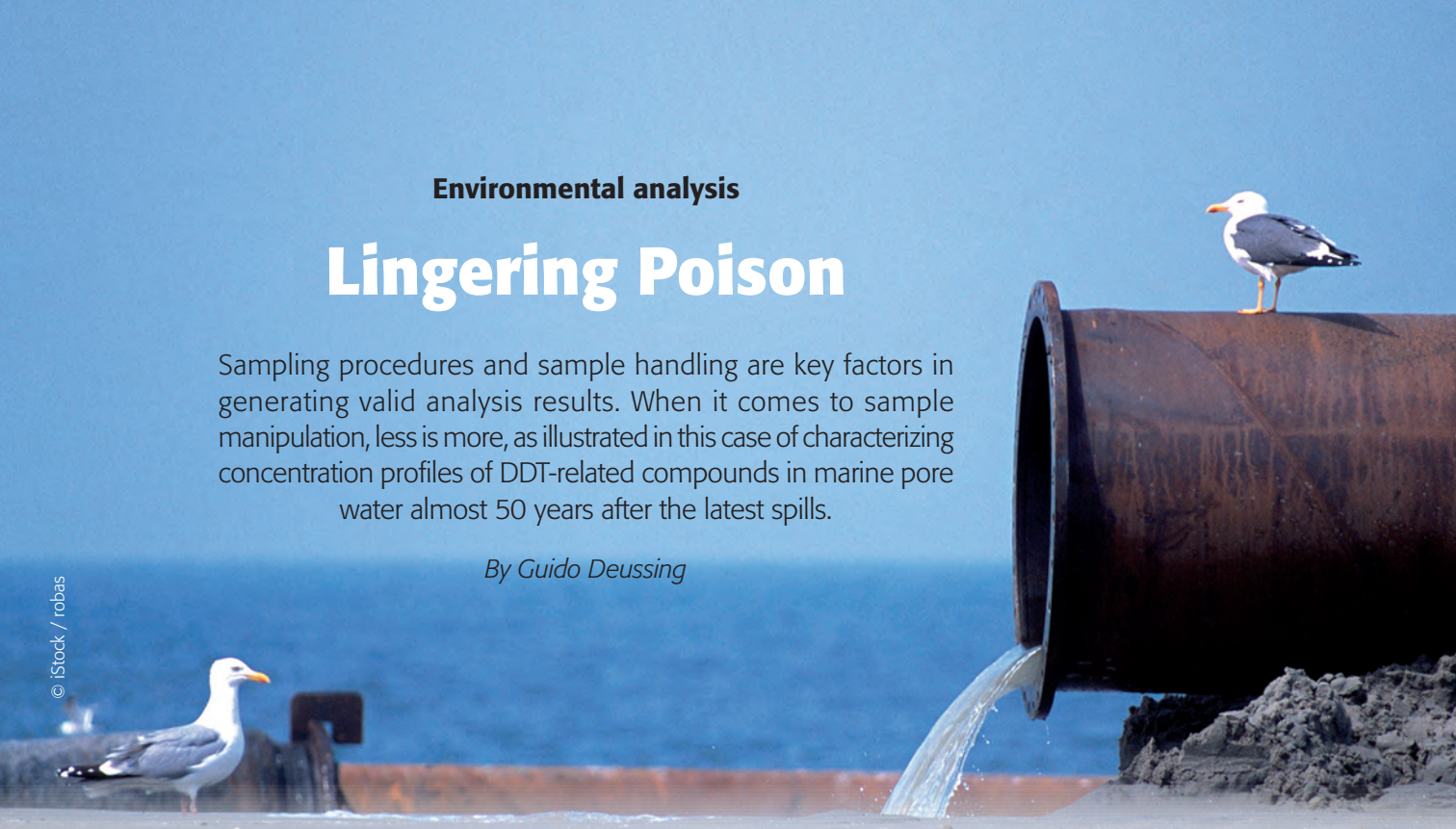
Lingering Poison

Sampling procedures and sample handling are key factors in generating valid analysis results. When it comes to sample manipulation, less is more, as illustrated in this case of characterizing concentration profiles of DDT-related compounds in marine pore water almost 50 years after the latest spills.

By Guido Deussing



When bodies of water are found to contain pollutants, it may not necessarily be a result of ongoing or recent contamination. It could be related to past spills that occurred during a time when "dilution" was considered an acceptable means of disposing chemical waste. Unfortunately, these persistent organic pollutants (POPs) can be adsorbed on sediment particles and then can slowly and steadily return to the marine ecosystem over a long period of time. If you want to assess the degree of contamination in any part of the ocean floor in order to appraise the risk of contamination of aquatic ecosystems, the bioavailability of contaminants in the sediment must be determined. U.S. scientists Robert P. Eganhouse and Erica L. DiFilippo successfully developed a new method for determination of ten DDT-related compounds in marine pore water based on extraction with disposable PDMS-coated fused silica fibers. After extraction, the analytes on the fibers were determined using automated Thermal Desorption GC/MS (TD-GC/MS). As they report in their journal paper, the method is simple, and "improves the ability to meet quality objectives at a significantly lower cost" [1].

Characteristics of sampling procedures

As part of a multi-disciplinary investigation of the factors controlling the fate of DDT in sediments of the Palos Verdes Shelf in the Pacific Ocean near Los Angeles, it was the task of Eganhouse and DiFilippo to assess the whereabouts and fate of the insecticide dichlorodiphenyltrichloroethane (DDT), which was prohibited in the US in 1972. The project was called into life following public discussion of the need for highly cost intensive clean-up [2]. Between 1947 and 1971, the Montrose Chemical Corporation released waste water containing hundreds of tons of DDT from their plant into the county sewer system from where it was released into the ocean. Eganhouse and DiFilippo set about determining the concentrations of ten DDT-related compounds in marine sediment pore water. As a first step, they identified a suitable sampling procedure and analysis method, which would give accurate results while not being too labor intensive or time consuming and preferably keeping cost and environmental impact to a minimum. Samples were taken slightly above the ocean floor and from ocean floor sediment. Sampling was conducted at three different locations on the Palos Verdes Shelf off the coast of Los Angeles, the scientists took sediment cores at a water depth of 60 meters using specially designed coring boxes. Subcores were subsequently taken using core tubes with sealed ports along their lengths for later insertion of analyte sampling devices. The cores were finally sealed at both ends and overlying seawater was expelled through a vent hole. The whole process was performed without compacting the core or altering its composition or structure, as Eganhouse and DiFilippo report. The cores were kept cool at the original sediment temperature (11 °C) and transported to the Laboratories of the United States Geological Survey (USGS) Water Science Center in San Diego, where they were stored in vertical position at a temperature of 11 °C until they could be sampled.

Extraction with disposable fibers

Eganhouse and DiFilippo succeeded in preserving the original sample structure and in avoiding changes to the natural distribution of contaminants between pore water and sediment in the sample. The scientists then focused their attention on determining the DDT related compound concentrations in the pore water. The next step was to extract and concentrate the analytes on a suitable carri-

er material for later analysis by TD-GC/MS. The extraction technique of choice was solid phase microextraction (SPME) and after several test runs, they decided to use 10 cm long pieces of fused silica fiber coated with a thin layer of polydimethylsiloxane (PDMS) (Fiberguide, Dr. M. T. O. Jonker). An important criterion was that the extractive capacity of the fibers should not disturb the system by significantly depleting the sample of contaminants. The fibers were inserted into the core through holes on the side, which were resealed, and were left for up to 79 days in order to allow equilibrium to be established between the fiber, pore water and sediment. Fibers were recovered after different extraction periods and prepared for TD-GC/MS analysis: They were rinsed, dried and cut in 2 cm long pieces that were placed in micro-vials and stored contamination free at -20 °C until they could be analyzed.

Intuitive Software Control

Open micro-vials, each containing three pieces of a single SPME fiber, were transferred to individually sealed glass thermal desorption tubes. The TDU tubes were fitted with transport adapters for automated processing using the GERSTEL MultiPurpose Sampler (MPS). Thermal desorption of the SPME fibers was performed using a GERSTEL Thermal Desorption Unit (TDU) connected to a Cooled Injection System (CIS), which was used for cryofocusing and subsequent transfer to the GC column for highly sensitive GC/MS determination. The intuitive MAESTRO software control enabled Eganhouse and DiFilippo to quickly set up and automate processing of the samples as well as automating spiking of the TDU tubes with liquid calibration standards or adding internal standard. The CIS was used to transfer analytes to the GC column inside the 6890 GC plus (Agilent Technologies) using programmed temperature vaporization (PTV). Separation was performed on a 30 m DB 5 capillary column, 0.25 mm ID and 0.25 µm film thickness, which was connected to the mass selective detector (5973 MSD from Agilent Technologies) through a heated interface kept at 275 °C. The quadropole was kept at 150 °C and the ion source at 230 °C.

Data acquisition was performed in full scan mode (FS) ranging from 50 to 500 amu at 1.68 scans per second. Setup and control of the MPS-TDU-GC/MS system as well as data acquisition and processing was performed using the MAESTRO software integrated with Agilent® Technologies ChemStation.

Verification of individual compound identities was based on MS and retention time data as well as comparisons with mass spectra in the NIST MS library database, Eganhouse and DiFilippo report.

Reaching the set goals

Following extended method development, during which Eganhouse and DiFilippo worked out the best extraction medium for the analysis and optimized desorption and analysis conditions, the scientists succeeded in determining ten DDT-related compounds in marine pore water using their TDU-GC/MS system. Among the analytes were: 4,4‘-DDNS, 4,4‘-DDNU, 4,4‘-DDMU, 2,4‘-DDE, 4,4‘-DDMS, 4,4‘-DDE, 2,4‘-DDD, 4,4‘-DDD, 2,4‘-DDT, and 4,4‘-DDT.

Method Detection Limits (MDLs) for all DDT-related compounds in the fiber coating were in the range between 0.177 ng/µL (4,4‘-DDNS) and 1.66 ng/µL (4,4‘-DDT) in FS and between 1.90 pg/µL (4,4‘-DDNS) and 4.98 pg/µL (4,4‘-DDT) in single ion monitoring mode (SIM). These units are per µL fiber coating, which translates to MDLs in seawater of 0.05–2.4 ng/L and 0.67–16 pg/L for FS and SIM respectively, calculated based on compound-specific PDMS-water partition coefficients at 11 °C. It should be noted that the GC/MS system used was an older model; current models will provide at least an order of magnitude better sensitivity and thus should generate significantly better MDLs.

In addition to the DDT-related compounds, other hydrophobic organic contaminants (HOCs) can be determined at sub-parts per trillion levels and monitored over extended time periods using the presented method. In their work analyzing marine pore water, Eganhouse and DiFilippo found the dominant contaminants to be 4,4‘-DDNU, 4,4‘-DDMU, 4,4‘-DDE and 2,4‘-DDE. Furthermore, a range of other compounds, both of natural and anthropogenic origins, were identified, among which were fatty acids, steroids, tensides, gasoline additives, antioxidants, plasticizers, and polychlorinated biphenyls (PCBs).

Performance data on the final method confirmed the high quality of the overall SPME-TD-GC/MS method used. The authors concluded that the method is relatively simple, cost effective, efficient, accurate and precise. Method recovery can be adjusted quite easily by adjusting the length of fiber inserted for analyte extraction and, as a precaution, multiple fibers can be inserted in each section in order to have a back-up sample in case of loss or breakage. Finally, the following statement from the authors should speak for itself: “Moreover, the TDU-CIS system appears to be effectively inert; we detected little or no evidence of degradation of these thermally sensitive compounds”.

References

[1] Robert P. Eganhouse, Erica L. DiFilippo, Determination of 1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl] benzene and related compounds in marine pore water by automated thermal desorption gas chromatography/mass spectrometry using disposable optical fiber, Journal of Chromatography A, 1415 (2015) 38–47

[2] www.scientificamerican.com/article/the-mystery-of-the-vanishing-ddt-in-the-ocean-near-los-angeles